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Anodic Disintegration of Zinc Undergoing

Electrolysis in Nitrate Solutions

by

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Abstract

A dark corrosion product forms on zinc during electrolysis in nitrate solutions but does not form when the electrode is amalgamated or when it is dissolved in chloride or sulfate solutions. Optical and x-ray studies revealed that the dark film is composed of many small metallic zinc particles embedded in a matrix of $\text{Zn}(\text{OH})_2$. During electrolysis this film spalls off the electrode and reacts with the electrolyte, subsequently turning white. It is concluded that the normal valency of zinc ion does not change during anodic dissolution in nitrate solutions, but rather that the apparent valency of less than two arises as a consequence of partial disintegration of the anode. The small metallic particles may then directly or indirectly reduce the oxidizing electrolyte. The dissolution of zinc outside the electrical circuit thus accounts for the lower coulombic equivalent.

Introduction

The nature of the mechanism of anodic dissolution of metals like Be, Mg, Al, Zn, and Cd in aqueous salt solutions has been, and continues to be, a problem of more complexity than a first glance would suggest. To explain the discrepancy between coulometric data and weight loss of metal electrodes in certain salt solutions, one school of investigators has proposed that the metals enter solution with valencies of less than two¹⁻⁵).

In the case of Be, a residue of Be metal is observed in the anolyte. This was credited to nucleation of Be arising from a disproportionation⁵⁾ of Be^{+1} to form Be^0 and Be^{+2} . More recently Straumanis and Mathis⁶⁾, using optical methods with high magnifications, clearly established that Be metal aggregates in the anolyte did not result by reaction but rather from disintegration of the anode. Optical examination of the metal electrode and of the metallic residue showed large numbers of deformation twins, thus establishing the origin of the residue. This mechanism thus explained why metal losses outside the faradaic current resulted in apparent valencies of less than normal, and why monovalent Be^+ ions could not be proved in the solution. Similarly Mg has been observed to undergo disintegration during electrolysis⁷⁾.

Sorenson et al³⁾ reported that upon electrolysis of zinc

and cadmium only bipoisitive ions formed at the anodes in the absence of oxidizing agents. However, they found that in nitrate and perchlorate solutions both zinc and cadmium exhibited mean initial valencies of less than two. Their experimental results were also confirmed in a recent study⁸⁾ of the anodic dissolution of zinc. However, when amalgamated zinc anodes (saturated) were employed in nitrate solutions only bipoisitive ions were formed and no nitrite ion could be detected after prolonged electrolysis. The presence of a gray-black film was reported to form on zinc during electrolysis in nitrate solutions but not on zinc in sulfate or chloride solutions. It did not occur on an amalgamated electrode in a nitrate solution.

Concluding that the film might be responsible for the apparent valencies of less than two, a study of the makeup and composition of the film was made. From the results it is evident that the apparent valencies arise as a result of disintegration of the anode. An alternative mechanism consistent with the experimental data is offered in lieu of that proposed by Sorenson et al³⁾.

Preparation and Identification of Surface Films

Electrolysis of pure zinc (99.995%) was carried out in an open cell in 3% KNO_3 . The current was varied from 20 to 100 ma cm^{-2} . The metal surface became completely covered

with a black film after about thirty seconds. At current densities ranging from 50 to 100 ma cm⁻². Small portions of the film spalled off the surface, immediately turning white.

In order to isolate the dark film and prevent its reaction with the anolyte, the electrode was immersed into dry acetone immediately following electrolysis. This successfully prevented hydrolysis. After immersion in the acetone some of the film flaked off the electrode and was collected. It proved to be stable for several months. A portion of this dark film was viewed optically using oil immersion at 850 magnification. In reflected light, a multitude of bright metallic particles were observed in a matrix of the corrosion product. The size of these particles was of the order of 10⁻⁵ cm. The accompanying photomicrograph (Fig. 1) shows these metallic particles in the film. Observations were also made of a portion of the deposit using oil immersion at 1430 magnification. In transmitted light some regions were black whereas in reflected light the corresponding regions appeared as bright, highly reflecting particles (Figs. 2 and 3). As another means of identification the darkest flakes were subjected to x-ray analysis using Cu K radiation. An aluminum screen was employed to eliminate fluorescence which originally covered several lines. The analysis yielded values for "d" spacings corresponding to the values for metallic zinc and

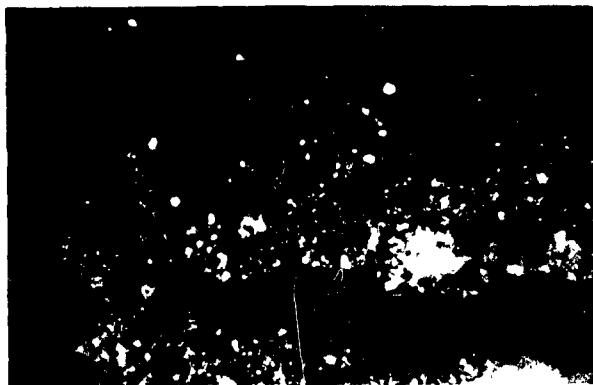


Fig. 1

Zinc particles in film formed during
anodic dissolution of zinc in 3% KNO_3
at 25°C. (850x)



Fig. 2

Zinc particles in the film as they
appear in transmitted light (1430x).



Fig. 3

Zinc particles in the film as they
appear in reflected light (1430x).

$\text{Zn}(\text{OH})_2$ (Table 1). The first two diffraction lines for $\text{Zn}(\text{OH})_2$ were partially shielded by fluorescence which could not be entirely eliminated.

Table I

Identification of film composition formed during anodic dissolution of zinc in 3% KNO_3 at 25°C

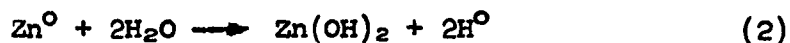
Experimental			ASTM	
"d" spacings in Å	I/I ₀		"d" spacings in Å	I/I ₀
Zn	2.08	100	2.09	100
Zn	2.47	45	2.47	53
Zn	2.31	40	2.31	40
$\text{Zn}(\text{OH})_2$	4.39	20 ¹⁾ 2)	4.38	100
$\text{Zn}(\text{OH})_2$	3.29	10 ¹⁾	3.27	80
$\text{Zn}(\text{OH})_2$	2.72	15 ²⁾	2.71	50

1) Fluorescence shielded lines. 2) I/I₀ relative to the Zn line (2.08) assigned relative intensity of 100.

Suggested Mechanism

The fact that zinc particles are expelled from the anode embedded in a hydroxide matrix, suggests that the reaction of zinc in nitrate solutions is film controlled in a manner similar to that proposed for magnesium^{9,10)}. The film which continuously spalls off the electrode surface contains many small metallic particles which, because of their size, are very active and are oxidized immediately by nitrate ion or by water to form insoluble $\text{Zn}(\text{OH})_2$ followed by oxidation of hydrogen to water as given by the following equations:





The stoichiometry of the net equation (2) and (3) and their sum, is equivalent to equation (1).

To establish the consistency of the proposed mechanism with the experimental results, a zinc anode was dissolved in 200 ml. of 3% KNO_3 at a current density of 57 ma cm^{-2} at a temperature of 51°C for a period of 1860 sec. Then the circuit was opened, the electrodes removed, and the solution containing insoluble $\text{Zn}(\text{OH})_2$ was allowed to stand until it was clear (about 10 hrs.). The Ph was measured and found to be 8.70. The weight of zinc dissolved in the aqueous phase was determined by titration of aqueous aliquots with EDTA. The precipitate was dissolved by adding 0.30M nitric acid. Aliquots were again withdrawn, titrated, and the total weight loss of the zinc electrode determined. This was done for two separate runs. Assuming that the difference between the normal valence state and the apparent valence state was entirely a consequence of zinc particles reacting outside the electrical circuit, the amount of $\text{Zn}(\text{OH})_2$ formed according to equation (1) was calculated to be 0.05751 g. This compared to a value of 0.05716 g obtained by difference from titration of the two solutions, before and after dissolving the precipitate. The weight of the zinc in the aqueous phase at a pH of 8.70, as calculated from the solubility

product ($K_{sp} = 5 \times 10^{-17}$), could be neglected. Considering that some film containing zinc particles still remained on the anode, the results are quite satisfactory.

The amount of nitrite ion formed was then calculated on the basis of equation (1) to be 0.00445 g. The amount of nitrite ion formed during two separate runs was determined by titration with $KMnO_4$ to be 0.00440 and 0.00455 g (each value - an average of 3 samples) in excellent agreement with the calculation.

Therefore, the reducing power of the products of electrolysis causing the reduction of nitrate to nitrite ions can be attributed to the presence of zinc particles dissolving outside the electrical circuit.

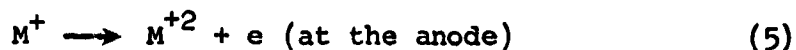
Discussion and Conclusions

The experimental results of this study and of a previous one⁸⁾ are in complete agreement with those of Sorenson et al, using a closed cell³⁾. As a mechanism they proposed that the primary reaction at the metal anode consists of a step-wise oxidation, the first step being oxidation of the metal to the unipositive ion:

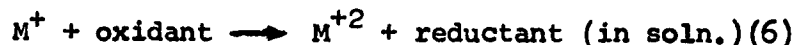


The unipositive ion being unstable will readily form the bi-positive ion in one of two ways: by further electrolytic oxidation at the anode, or by chemical oxidation by the

oxidizing agent in solution. Therefore, the second step might be either



or



With non-reducible electrolytes reaction (6) cannot occur and consequently an initial mean valence of two according to reaction (5) would be observed. With reducible electrolytes, however, the two possible mechanisms of the second step are competitive; which one predominates depends on the nature of the oxidant and the conditions of the experiment. The mean valence might then range from +1 to +2 depending upon the relative extents of reactions (5) and (6) which in turn depend upon the concentration of the oxidizing electrolyte and the temperature. The rate of reaction (6) would be expected to increase with increasing concentration of the oxidant and temperature. Their attempts, however, to qualitatively detect the presence of unipositive species were unsuccessful and the gray-black film formed on zinc in NaNO_3 was only mentioned.

While their proposed mechanism is consistent with their experimental results, except the film formation, the alternative mechanism suggested in this study is also consistent with the experimental data but does not require the postulation of intermediate valence states. To the best knowledge

of the authors, no electron paramagnetic resonance studies have reported the presence of Mg^{+1} , Zn^{+1} . etc. in aqueous solutions. Yet disintegration of anodes has been known for many years and existence of metallic particles has been confirmed in this and other studies. Therefore, if a film containing large numbers of dispersed particles spalls off the electrode and the particles directly or indirectly react with the oxidant outside the electrical circuit one must of necessity calculate an apparent or fictitious valence of less than normal and also observe the presence of a reductant. The mechanism suggested in this study (equations 1, 2 and 3) is similar to that suggested by Hoey and Cohen⁹⁾ for anodic dissolution of Mg in neutral salt solutions and also finds support in the work of other investigators¹¹⁻¹³⁾. The rate at which the film is expelled from the surface of the metal might be expected to increase with temperature explaining the lower values for the apparent valence at higher temperature.

References

- (1) Epelboin, I., Z. Elektrochem., 59, 689 (1955).
- (2) Petty, R.L., A.W. Davidson, and J. Kleinberg, J. Amer. Chem. Soc., 76, 363 (1954).
- (3) Sorenson, O.T., A.W. Davidson, and J. Kleinberg, J. Inorg. Nucl. Chem., 13, 64 (1960).
- (4) Raijola, E. and A.W. Davidson, J. Amer. Chem. Soc., 78, 556 (1956).

- (5) Laughlin, B.D., J. Kleinberg, and A.W. Davidson, J. Amer. Chem. Soc., 78 559 (1956).
- (6) Straumanis, M.E., and D.L. Mathis, J. Less-Common Metals, 4, 213 (1962).
- (7) Straumanis, M.E. and B.K. Bhatia, J. Electrochem. Soc., 110, 357 (1963).
- (8) James, W.J. and G.E. Stoner, J. Amer. Chem. Soc., 85, 1354 (1963).
- (9) Hoey, G.R. and M. Cohen, J. Electrochem. Soc., 105, 245 (1958).
- (10) James, W.J., M.E. Straumanis, B.K. Bhatia, and J.W. Johnson, J. Electrochem. Soc., 110, (1963) in press.
- (11) Robinson, J.L. and P.F. King, J. Electrochem. Soc., 108, 36 (1961).
- (12) Higgins, W.E., J. Electrochem. Soc., 105, 737 (1958).
- (13) Roald, B. and W. Beck, J. Electrochem. Soc. 98, 227 (1951).